

SPECIFICATION AMENDMENTS

On page 1, insert above line 1, insert--Priority Claim

The present application claims priority on European Patent Application 03076114.2 filed 15 April 2003. –

On page 1, please replace the first paragraph as follows:

The invention ~~is directed~~ relates to a process to prepare a mixture comprising carbon monoxide and hydrogen from a carbonaceous feed by performing a partial oxidation reaction and an endothermic steam reforming reaction.

On page 2, please replace the paragraph at lines 25-30 as follows:

~~The object of the present invention is~~ It would be useful to provide a process wherein the CSR reactor can be operated at a lower steam to carbon ratio and wherein the methane content in the resulting synthesis gas is kept at a lower level such that the synthesis gas can be used for example advantageously as feed for a Fischer-Tropsch reaction.

On page 2, please replace the paragraph beginning at line 32 and ending on page 3, line 22 as follows:

~~This object is achieved with the following process.~~

The invention provides a process ~~process~~ for the preparation of hydrogen and carbon monoxide containing gas from a carbonaceous feedstock, ~~the process comprising:~~ by performing the following steps:

(a) ~~partial oxidation of~~ partially oxidizing a carbonaceous feedstock in a vertically oriented tubular partial oxidation reactor vessel comprising a burner at

its upper end thereby obtaining a first gaseous mixture of hydrogen and carbon monoxide,

(b) ~~catalytie~~ catalytically steam reforming a carbonaceous feedstock in a Convective Steam Reformer comprising a tubular reactor provided with one or more tubes containing a reforming catalyst, wherein the steam to carbon molar ratio of the feed to step (b) is below 1, to obtain as separate product a steam reforming product,

(c) feeding the steam reformer product to the upper end of the partial oxidation reactor to obtain a mixture of the effluent of step (a) and the steam reformer product, and

(d) providing the required heat for the steam reforming reaction in step (b) by convective heat exchange between the mixture obtained in step (c) and the steam reformer reactor tubes thereby obtaining a hydrogen and carbon monoxide containing gas having a reduced temperature.

~~Applicants found that by~~ By feeding the steam reformer effluent obtained in step (b) to the upper part of the partial oxidation reactor vessel a large portion of the unconverted methane is converted to carbon monoxide and hydrogen due to the fact that methane will be partially oxidized by the burner also present in that part of the partial oxidation reactor vessel.

On page 3, please delete line 30.

On page 3, above line 31, please insert the following:

Brief Description of the Figures

On page 5, please replace the paragraph beginning on line 28 and ending on page 6, line 7 as follows:

Step (b) may be performed by well-known steam reforming processes, wherein steam and the gaseous

hydrocarbon feed are contacted with a suitable reforming catalyst in a CSR reactor. The convective steam reactor preferably comprises of a tubular reactor vessel provided with one or more tubes containing a reforming catalyst. Various designs for such a reactor are known and suited for the present invention. The design should be such that the steam reformer product and the synthesis gas used to provide heat are obtained as separate streams in such a reactor. Examples of such a reactor concept is described in US[[-A-]] Pat. No. 6224789, which is herein incorporated by reference. Alternatively a design such as illustrated in Figure 1 may be applied.

On page 8, please replace the paragraph from lines 1-30 as follows:

The catalyst and process conditions as applied in the steam reformer reactor tubes may be those known by the skilled person in the field of steam reforming. Suitable catalysts comprise nickel optionally applied on a carrier, ~~for~~ for example alumina. The space velocity of the gaseous feed is preferably from 700 to 1000 litre liter(S.T.P.)/litre liter catalyst/hour, wherein S.T.P. means Standard Temperature of 15 °C and pressure of 1 bar abs. The steam to carbon (as hydrocarbon and CO) molar ratio is below 1 and preferably from 0.5 up to 0.9. If such low steam to carbon ~~ratio's~~ ratios are applied in step (b) the catalyst preferably comprises a Group VIII metal. More preferably the catalyst comprises (a) an oxidic support material and (b) a coating comprising between about 0.1 and about 7.0 wt% of at least one of the metals of the group consisting of Pt, Ni, Pd and Co, preferably platinum; said support material comprising: (i) at least 80 wt% of ZrO₂ which has been calcined at a temperature up to about 670 °C before the application of

said coating; (ii) 0.5-10 mol% of at least one oxide selected from the group consisting of oxides of Y, La, Al, Ca, Ce and Si, preferably La_2O_3 . Examples of such catalysts are include, for example, the catalyst described in EP-A-695279. Preferably the feed also comprises an amount of CO_2 , wherein preferably the CO_2 over carbon (as hydrocarbon and CO) molar ratio is from 0.5 up to 2. The product gas of step (b) preferably has a temperature of from 600 up to 1000 °C and an H_2/CO molar ratio of from 0.5 up to 2.5.

On page 9, please replace the first full paragraph on lines 5-15 as follows:

Optionally the mixture of the effluent of step (a) and the steam reformer product as obtained in step (c) may be subjected to [[a]] an autothermal reformer step, also referred to as post catalytic reformer step, at the elevated temperatures of said mixture to convert the gaseous mixture obtained in step (c) to a mixture having a H_2/CO molar ratio closer to the desired thermal equilibrium H_2/CO molar ratio values valid for said operating temperatures. The combined mixture, optionally after performing such a post reforming step, is used in step (d).

On page 9, please replace the paragraph beginning on line 24 and ending on page 10, line 10 as follows:

Preferably the steam reformer product (55) is fed close, i.e. in the upper half of vessel (51), to the burner (52) in order to benefit the most ~~ef~~ from the resultant elevated temperatures of from 800 up to 1050 °C present in that region of the vessel (51). The methane content in steam reformer product (55) may be between 5 and 30 mol% carbon relative to the carbon as hydrocarbon

in the feed to step (b), (43). This relatively high methane content ~~is a resultant~~ results when operating step (b) at low steam to carbon ratio as described before. Because a methane slip will be corrected by the process of the current invention a lower reaction temperature in the CSR reactor tubes may also be allowed. A lower reaction temperature will also result in ~~than~~ that more non-reacted methane will be part of product (55). Low temperatures in step (b) are suitably between 700 and 800 °C as measured on steam reformer product (55) as it leaves the reactor (44). A low temperature is desirable for material strength reasons for the internals used in reactor (44).

On page 11, please replace the first full paragraph on lines 6-22 as follows:

The invention is especially directed to the above process for the preparation of hydrogen and carbon monoxide containing gas (synthesis gas), wherein additional steps (e) (f) and (g) are also performed. In step (e) the synthesis gas is catalytically converted using a Fischer-Tropsch catalyst into a hydrocarbons comprising stream. In step (f) the hydrocarbons comprising stream of step (e) is separated into a hydrocarbon product and a gaseous recycle stream. Suitably the hydrocarbon product ~~are~~ these comprise hydrocarbons having 5 or more carbon atoms, preferably having 4 or more carbon atoms and more preferably having 3 or more carbon atoms. The gaseous recycle stream may comprise normally gaseous hydrocarbons produced in the synthesis process, nitrogen, unconverted methane and other feedstock hydrocarbons, unconverted carbon monoxide, carbon dioxide, hydrogen and water.

On page 11, please replace the paragraph beginning on line 31 and ending on page 12, line 6 as follows:

Step (e) and (f) may be performed by the well known Fischer-Tropsch processes which are for example the Sasol process and the Shell Middle Distillate Process. Examples of suitable catalysts are based on iron and cobalt. Typical reactor configurations include slurry reactors and tubular reactors. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US[-A-] Pat. No. 4943672, US[-A-] Pat. No. 5059299, WO-A-9934917 and WO-A-9920720, all of which are herein incorporated by reference.

On page 12, please replace the paragraph beginning on line 30 and ending on page 13, line 3 as follows:

The following examples will illustrate how the reactor according the invention may be used in a process to make produce a mixture of carbon monoxide and hydrogen. The values presented are calculated values. These will come close to the actual values because use has been made of well known thermodynamic relations known to the skilled person in the field of gasification and steam reforming.

On page 20 above line 1, insert --We claim:--